

determined by a differential scanning calorimeter of <160°C, and 20-40% by weight of a polyethylene resin (C). The crosslinked polyolefin resin foam can be obtained by molding the polyolefin resin composition into a desired shape and then foaming/crosslinking the resin.

**Method for Preparing Formed Polyurethane Foam Materials and Formed Polyurethane Foam Materials Therefrom**

*Document Number:* EP1721720

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This invention relates to a novel method for the preparation of polyurethane foam materials suited for seamless breast pads, cups, fronts, and the like for use in brassieres and other garments. Polyurethane foam is produced from aliphatic isocyanates and polyols. The aliphatic polyurethane foam is reticulated to remove all celled membranes and sliced into sheet with a thickness greater than the thicker wall of the finished brassiere cup. The sliced aliphatic polyurethane foam sheet is then pressed between mold parts of a female mold part and a male mold part. The mold parts are closed and pressed whereby the aliphatic polyurethane foam material is molded into the exact shape of the mold cavity. The molded aliphatic polyurethane foam material can be used as seamless breast pads, cups, fronts, and the like in brassieres and other garments.

and expresses superior non-yellowing properties over previous aromatic polyurethane brassiere pads and improved breathability and porosity.

**Low-resilience Soft Polyurethane Foam and Method for Producing the Same**

*Document Number:* WO2006115169

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Disclosed is a soft polyurethane foam using no plasticizer which is excellent in low resilience and durability while having high air permeability. This soft polyurethane foam shows only a small change in hardness when the temperature changes. Specifically disclosed is a method for producing a soft polyurethane foam wherein a polyol mixture containing polyols (A) and (B) and monool (D) and a polyisocyanate compound are reacted at an isocyanate index of not less than 90 in the presence of a foaming agent or the like. The polyol (A) is a polyol having an average of 2-3 hydroxyl groups and a hydroxyl number of 10-90 mg KOH/g which is obtained through ring-opening addition polymerization of an alkylene oxide using a composite metal cyanide complex catalyst. The polyol (B) is a polyol other than the polyol (A) which has an average of 2-3 hydroxyl groups and a hydroxyl number of 15-250 mg KOH/g. The monool (D) is a monool having a hydroxyl number of 10-200 mg KOH/g.

# Thin Microcellular Plastic Sheet Incorporating Designed Foaming Patterns Made by Photochemical Foaming Technology\*

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**ABSTRACT:** A novel chemical foaming technology is proposed to manufacture microcellular plastic sheet with a thickness of 100  $\mu\text{m}$  or less. A foamable plastic consisting of a polymer with *t*-butyl ester groups and a photoacid generator has been developed. Upon ultraviolet irradiation, the photoacid generator releases protons. The protons transform the *t*-butyl ester group attached to the polymer into isobutene gas upon heating, which leads to controlled microcellular formation in the plastic film. The cell size and the cell density of the microcellular plastic are controlled by ultraviolet irradiation and the heating temperature. By adjusting these two parameters, the optical properties of the resulting microcellular plastic can be predetermined. A thin microcellular sheet that has a micron-order foaming pattern exhibiting different transparencies has been produced by using a pattern mask.

**KEY WORDS:** thin microcellular plastic sheet, designed foaming pattern, *t*-butyl ester group, isobutene gas, optical devices.

## INTRODUCTION

Microcellular plastics (MCPs) are unique plastics containing many hollow cells of 10  $\mu\text{m}$  or less in diameter. A physical foaming method using supercritical carbon dioxide ( $\text{CO}_2$ ) has generally been used to produce MCPs [1-6]. However, manufacturing a thin MCP sheet of 100  $\mu\text{m}$  or less in thickness by this method has been difficult, because the  $\text{CO}_2$  gas produced in such a thin sheet easily escapes from the surface.

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Figures 1 and 8-6 appear in color online: <http://foal.sagepub.com>

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A new methodology for manufacturing thin MCP sheet was proposed in an earlier study [7]. This method is a chemical foaming method which takes advantage of the photochemical-induced chemical reaction of a photoresist [8]. In this method, the foamable material is composed of a mixture of a photoacid generator and a polymer with *t*-butyl ester groups.

The foaming mechanism is shown in Figure 1. First, protons are generated from the photoacid generator upon ultraviolet irradiation. When the UV-irradiated plastic is heated, the protons decompose the *t*-butyl ester group into isobutene gas. The gas leads to MCP formation in the plastic sheet.

This novel foaming technology produces new MCPs and applications, such as thin sheet with submicron-sized cells and patterned optical devices, which are impossible to make by the conventional foaming method.

## EXPERIMENT

The composition of the foamable material is a mixture of poly(*tert*-butylacrylate-co-methylmethacrylate) with an average molecular weight of about 300,000, and diphenyliodonium perfluoro-1-butanedisulfonate (a photoacid generator). A thin MCP sheet was prepared by the following three steps.

### (1) Sheet preparation

A solution of the foamable material dissolved in an organic solvent was coated on one side of a poly(ethylene terephthalate) (PET) sheet.

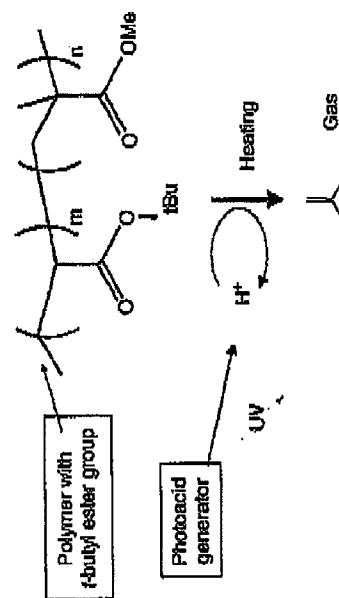


Figure 1. Novel chemical foaming mechanism.

## EXHIBIT A

The coated layer was dried at 100°C in a dry oven. The dried free-standing sheet of foamable material was manually separated from the PET sheet.

### (2) Ultraviolet irradiation

The sheet was irradiated with an ultraviolet lamp. For pattern foaming, the sheet was exposed to UV light through a pattern mask.

### (3) Heating and foaming

After UV irradiation, the sheet was heated in a dry oven or on a heating stage to foam. The heating temperature was between 110 and 130°C.

The cell structure of the MCP sheet was examined by observing the cross section of the MCP sheet with a scanning electron microscope (SEM). Changes in chemical structure were examined by NMR measurement. Thermal properties were measured with a thermogravimetry-differential thermal analyzer (TG-DTA).

## RESULTS AND DISCUSSION

### Thin MCP sheet

Thin polymer sheets with a thickness of 35  $\mu\text{m}$  having cells of 0.4  $\mu\text{m}$  diameter were successfully prepared, as shown in Figure 2. The foaming ratio determined from the volume change was 1.2. The disappearance of

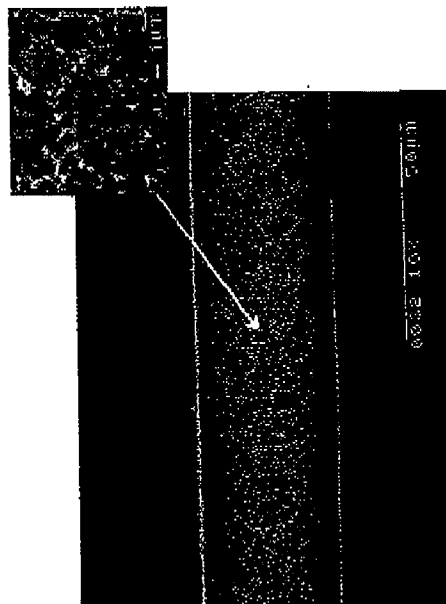


Figure 2. Cross section of a thin MCP sheet.

the *t*-butyl ester group was confirmed by NMR measurement. TG-DTA shows that the UV-exposed region was foamed at 80°C. On the other hand, the region not exposed to UV light did not experience any foam formation. The main backbone of the polymer was found to be intact.

Figure 3 shows the relation between the reflectance and the cell diameter in the MCP sheet. The experimental data showed that MCP with cell size of about 0.4  $\mu\text{m}$  presented the highest reflectance (a). This cell size of 0.4  $\mu\text{m}$  agrees well with the optimal cell diameter for maximum light scattering efficiency obtained by the calculation based on Mie scattering theory (b).

#### Thin Plastic Sheet with a Designed Foaming Pattern

The designed formation of foaming was attempted by this technology. Figure 4 shows the resulting MCP sheet with line and space patterns realized by UV light exposure through a pattern mask. The white lines

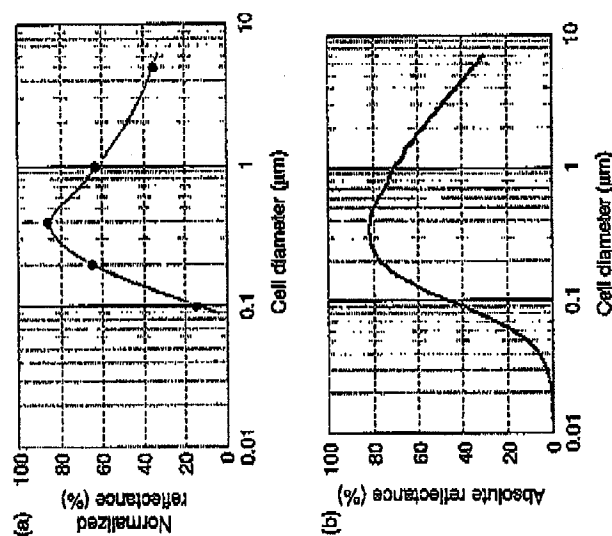


Figure 3. The relation between reflectance and cell diameter: (a) experimental data and (b) simulation based on Mie scattering theory.

## EXHIBIT A

are composed of foams. The maximum resolutions of 7 and 19  $\mu\text{m}$  for line width and spacing, respectively, were successfully achieved in this experiment.

Figure 5(a) shows an MCP sheet with a gradation pattern exhibiting a controlled continuous change from transparent to opaque. This foaming pattern was prepared by changing the amount of UV light exposure through a gradation mask. Figure 5(b) and (c) shows cross sections of two regions of different opacity, which implies that opacity of the sample is determined by the size of cells, not by the number of them.

By accumulating the films of the different foaming levels, the film having a controlled foam distribution in depth direction is manufactured. Figure 6 shows the cross-section of one of the resulting films, which is composed of a foamed surface layer (a, 30  $\mu\text{m}$  thickness) and no-foam contained layer (b, 350  $\mu\text{m}$  thickness). By applying this technique, multilayer-multifoam polymer sheets are obtained.

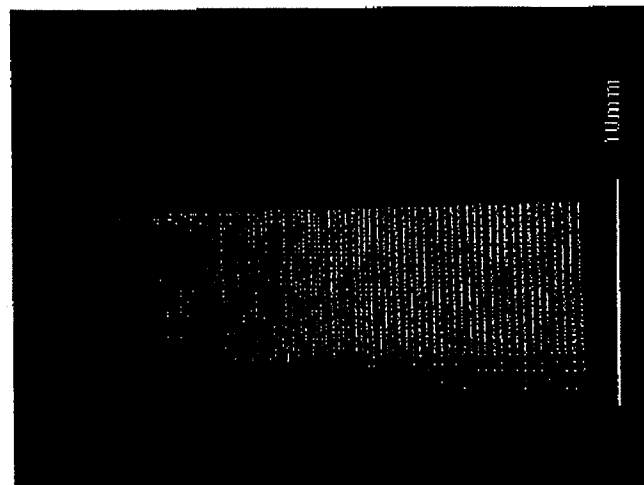


Figure 4. Line and space pattern of MCP photographed against a black background.

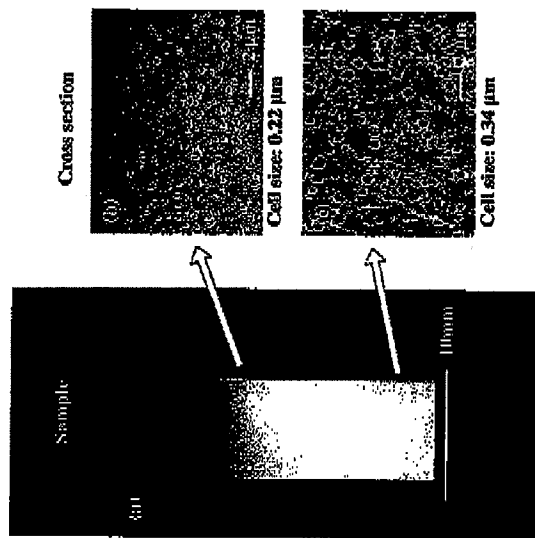


Figure 5. Gradation pattern of MCP.

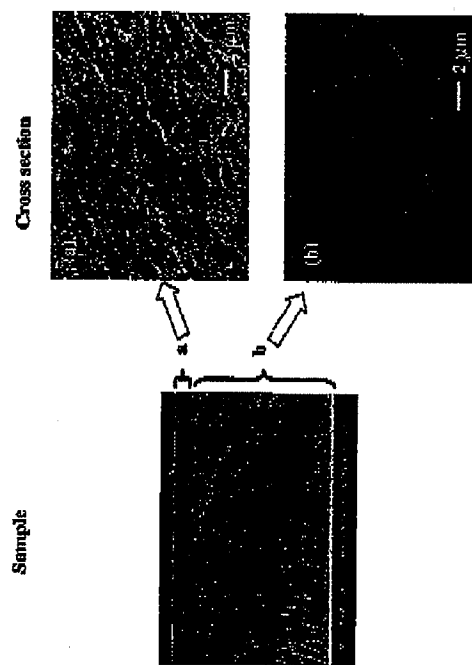


Figure 6. Cross section of a depth patterned MCP: (a) foam layer and (b) no foam layer.

## CONCLUSIONS

MCP sheets thinner than 100  $\mu\text{m}$  have been developed by a novel chemical foaming method using foamable material consisting of a polymer with *t*-butyl ester groups and a photoacid generator.

It has been proved, by adjusting UV light exposure and heating temperature, that one can produce thin plastic films with (a) high resolution foaming pattern, (b) smooth gradation of foam, and (c) controlled foaming in depth direction. These are just a few examples that prove the usefulness of this technology. The authors concentrate their work on fabricating optical devices, such as a designed diffusion film, a light guide panel, and an optical waveguide.

## REFERENCES

1. Martini, J.E., Suh, N.P. and Waldman, F.A. (1982). US Patent 4473665.
2. Calton, J.S. and Suh, N.P. (1987). Nucleation of Microcellular Foam: Theory and Practice, *Polym. Eng. Sci.*, 27(7): 500-503.
3. Kumar, V. and Suh, N.P. (1990). A Process for Making Microcellular Thermoplastic Parts, *Polym. Eng. Sci.*, 30(20): 1323-1329.
4. Ramesh, N.S., Rasmussen, D.H. and Campbell, G.A. (1994). The Heterogeneous Nucleation of Microcellular Foams Assisted by the Survival of Microvoids in Polymers Containing Low Glass Transition Particles. Part II: Experimental Results and Discussion, *Polym. Eng. Sci.*, 34(22): 1698-1706.
5. Baldwin, D.F., Shimbo, M. and Suh, N.P. (1995). The Role of Gas Dissolution and Induced Crystallization During Microcellular Polymer Processing: A Study of Poly(Ethylene Terephthalate) and Carbon Dioxide Systems, *J. Eng. Mater. Tech.*, 117: 62-74.
6. Baldwin, D.F., Park, C.H. and Suh, N.P. (1996). A Microcellular Processing Study of Poly(Ethylene Terephthalate) in the Amorphous and Semicrystalline States. Part I: Microcell Nucleation, *Polym. Eng. Sci.*, 34(11): 1437-1445.
7. Kojima, J., Takada, T. and Jinno, F. (2003). *Japan Society of Polymer Processing Symposium Papers*, #227, November 3-4.
8. Ito, H. and Willson, C.G. (1988). Chemical Amplification in the Design of Dry Developing Resist Materials, *Polym. Eng. Sci.*, 28(18): 1012-1018.